

**National Exposure Research Laboratory  
Research Abstract**

Government Performance Results Act (GPRA) Goal #2  
Annual Performance Measure #202

Significant Research Findings:

**Method Development for the Determination of  
Perchlorate in Drinking Water Using Ion Chromatography  
With Mass Spectrometric Detection****Scientific  
Problem and  
Policy Issues**

Perchlorate ( $\text{ClO}_4^-$ ) is both a naturally occurring and manmade chemical. It is used primarily as a solid oxidant in propellant products such as rockets, pyrotechnics, air bag inflators and highway safety flares. Perchlorate was found in drinking waters in the late 1990s and was placed in the EPA's Unregulated Contaminant Monitoring Rule (UCMR) in 1999 to gather nationwide occurrence data. Since that time, perchlorate has been found in drinking waters in 34 states. Perchlorate is a known thyroid hormone inhibitor. Thyroid hormones are critical for metabolism throughout life and are critical for proper fetal brain development. The EPA Reference Dose for perchlorate has not yet been determined, but the concentration of human health concern in drinking water may be lower than what the only approved EPA method for measuring perchlorate is capable of detecting (EPA Method 314.0). That method uses ion chromatography to separate the perchlorate ion from interfering ions followed by conductivity detection. Because conductivity is a non-specific parameter, confirmation of perchlorate is by retention time on the ion chromatography column. In 2002, the Office of Ground Water and Drinking Water (OGWDW) and the National Exposure Research Laboratory undertook a collaborative research effort to develop an analytical method for perchlorate with improved selectivity and sensitivity that would be available for use in the event perchlorate is regulated or if a second round of occurrence monitoring is performed.

**Research  
Approach**

Perchlorate in drinking water was separated from potential interferences using ion chromatography with a potassium hydroxide mobile phase. The eluate from the chromatographic column was passed through a conductivity suppressor to exchange the potassium ions of the mobile phase with hydrogen so that perchlorate in a matrix of pure water could be introduced into a mass spectrometer using an electrospray ionization interface. The measured response in mass spectrometry, mass-to-charge ratio ( $m/z$ ),

provides specific information about perchlorate. There are two perchlorate ions based on the 76% relative abundance of  $^{35}\text{Cl}$  ( $^{35}\text{Cl}^{16}\text{O}_4^-$ ,  $m/z = 99$ ) and the 24% relative abundance of  $^{37}\text{Cl}$  ( $^{37}\text{Cl}^{16}\text{O}_4^-$ ,  $m/z = 101$ ). Using an oxygen-18 enriched perchlorate internal standard, quantitation of perchlorate was performed using the  $m/z$  101 ion. Confirmation was made by verifying the  $m/z$  99/101 area count ratio and matching the retention time of the labeled internal standard.

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**Results and Impact**

This method (U.S. EPA Method 330.0), combining ion chromatography with mass spectrometric detection, allows detection, confirmation, and quantification of perchlorate in surface and ground waters sources, and in finished drinking waters, at concentrations of less than 1  $\mu\text{g/L}$ . The lowest concentration minimum reporting limit of this new method is 0.1  $\mu\text{g/L}$ , whereas, the minimum reporting limit of Method 314.0 is 4  $\mu\text{g/L}$ . In EPA's preliminary risk assessment, currently under review by the National Academy of Sciences, the concentration in drinking water protective of human health may be as low as 1  $\mu\text{g/L}$ . Massachusetts health officials have adopted this level and California has set a preliminary safety standard of 6  $\mu\text{g/L}$ . This new method for measuring perchlorate in drinking water at 0.1  $\mu\text{g/L}$  will meet EPA's data quality objectives in the future collection of nationwide occurrence data and support agency needs should a regulatory determination be made.

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**Research Collaboration and Research Products**

Hedrick, E., T. Behymer, R. Slingsby and D. Munch, "U.S. EPA Method 330.0: Determination of Perchlorate in Drinking Water by Ion Chromatography with Suppressed Conductivity and Electrospray Ionization Mass Spectrometry," National Exposure Research Laboratory, Microbiological and Chemical Exposure Assessment Research Division, Chemical Exposure Research Branch, 26 W. Martin Luther King Dr., Cincinnati, Ohio 45268.

Hedrick, Elizabeth and David Munch, "Measurement of perchlorate in water by use of an  $^{18}\text{O}$ -enriched isotopic standard and ion chromatography with mass spectrometric detection," *Journal of Chromatography A*, 1039, 2004, pp. 83-88.

Hedrick, E.J., "Overview of Proposed EPA Method 330.0: Determination of Perchlorate in Drinking Water by Suppressed Conductivity Ion Chromatography and Mass Spectrometric Detection," Invited Speaker at the Severn Trent 4th Annual Louisville Analytical Conference, Louisville, KY, June 8-9, 2004.

Hedrick, E.J. and T.D. Behymer, "Development of a Better Method to Identify and Measure Perchlorate in Drinking Water," Presented at the EPA Science Forum 2004, Washington, DC, June 1-3, 2004.

Hedrick, E.J., "Overview of a New EPA Method: Determination of Perchlorate in Drinking Water by Ion Chromatography, Suppressed Conductivity with Electrospray Ionization Mass Spectrometric Detection," Invited Speaker at the Texas Commission on Environmental Quality, Environmental Trade Fair and Conference, Austin, TX, May 3-5, 2004.

Hedrick, E.J., and D.J. Munch, "Sub-ppb Quantitation and Confirmation of Perchlorate in Drinking Waters Containing High Total Dissolved Solids Using Ion Chromatography with Mass Spectrometric Detection," Presented at the American Water Works Association Water Quality Technology Conference, Philadelphia, PA, November 2-6, 2003.

Hedrick, E.J. and D.J. Munch, "EPA Perchlorate Method Development Activities," Invited Speaker at the Joint IDQTF/DoD EDQW Roundtable State of the Art in Analysis of Perchlorate in Environmental Samples, Dallas, TX, October 23, 2003

Hedrick, E.J., and D.J. Munch, "Measurement of Perchlorate in Water Using an Oxygen-18 Enriched Isotope Standard and Ion Chromatography Mass Spectrometric Detection," Presented at the International Ion Chromatography Symposium, San Diego, CA, September 21-24, 2003.

Hedrick, E.J., "Methods Development to Improve Low-level Perchlorate Detection in Drinking Water by Conductivity and Mass Spectrometry - Issues and Impact," Invited Speaker at the Severn Trent 3rd Annual Analytical Conference, Louisville, KY, June 17-18, 2003.

Hedrick, E.J., R. Slingsby, D.J. Munch, and D.P. Hautman, "Low-level determination of perchlorate in drinking water using ion chromatography mass spectrometry," Presented at: 51st ASMS Conference, Montreal, Canada, June 8-12, 2003.

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**Future Research**

No further drinking water methods development work is required. Future work will focus on application of the developed method to other matrices of environmental interest such as high salinity waters and food grade chemicals.

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**Contacts for Additional Information**

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